

## CLAIMS

1. A process of making polytrimethylene ether glycol comprising:
  - (a) providing 1,3-propanediol reactant and polycondensation catalyst; and
  - (b) continuously polycondensing the 1,3-propanediol reactant to polytrimethylene ether glycol.
2. The process of claim 1 wherein the polycondensing is carried out in two or more reaction stages.
3. The process of claim 1 wherein the polycondensing is carried out at a temperature greater than 150°C.
4. The process of claim 3 wherein the temperature is greater than 160°C.
5. The process of claim 4 wherein the temperature is greater than 180°C.
6. The process of claim 1 wherein the polycondensing is carried out at a temperature less than 250°C.
7. The process of claim 6 wherein the temperature is less than 220°C.
8. The process of claim 7 wherein the temperature is less than 210°C.
9. The process of claim 3 wherein the temperature is less than 210°C.
10. The process of claim 1 wherein the polycondensation is carried out at a pressure of less than one atmosphere.
11. The process of claim 10 wherein the pressure is less than 500 mm Hg.
12. The process of claim 11 wherein the pressure is less than 250 mm Hg.
13. The process of claim 11 wherein the pressure is greater than 1 mm Hg.
14. The process of claim 12 wherein the pressure is greater than 20 mm Hg.
15. The process of claim 14 wherein the pressure is greater than 50 mm Hg.
16. The process of claim 1 wherein the 1,3-propanediol reactant is selected from the group consisting of 1,3-propanediol and/or dimer and trimer of 1,3-propanediol and mixtures thereof.
17. The process of claim 16 wherein the 1,3-propanediol reactant is selected from the group consisting of the 1,3-propanediol or the mixture containing at least 90 weight % of 1,3-propanediol.
18. The process of claim 16 wherein the 1,3-propanediol reactant is the 1,3-propanediol.
19. The process of claim 17 wherein the polycondensation pressure is between 50 and 250 mm Hg.
20. The process of claim 1 wherein the catalyst is homogeneous.

21. The process of claim 20 wherein the catalyst is selected from the group consisting of a Lewis Acid, a Bronsted Acid, a super acid, and mixtures thereof.
- 5 22. The process of claim 21 wherein the catalyst is selected from the group consisting of inorganic acids, organic sulfonic acids, heteropolyacids, and metal salts thereof.
- 10 23. The process of claim 1 wherein the catalyst is selected from the group consisting of sulfuric acid, fluorosulfonic acid, phosphorus acid, p-toluenesulfonic acid, benzenesulfonic acid, phosphotungstic acid, phosphomolybdic acid, trifluoromethanesulfonic acid, 1,1,2,2-tetrafluoroethanesulfonic acid, 1,1,1,2,3,3-hexafluoropropanesulfonic acid, bismuth triflate, yttrium triflate, ytterbium triflate, neodymium triflate, lanthanum triflate, scandium triflate and zirconium triflate.
- 15 24. The process of claim 1 wherein the catalyst is sulfuric acid.
25. The process of claim 1 wherein the catalyst is heterogeneous.
26. The process of claim 25 wherein the catalyst is selected from the group consisting of zeolites, fluorinated alumina, acid-treated silica, acid-treated silica-alumina, heteropolyacids and heteropolyacids supported on zirconia, titania, alumina and/or silica.
- 20 27. The process of claim 1 wherein the polycondensation is carried out in a reactor equipped with a heat source located within the reaction medium.
28. The process of claim 1 wherein the polycondensation is carried out in an up-flow co-current column reactor and the 1,3-propanediol reactant and polytrimethylene ether glycol flow upward co-currently with the flow of gases and vapors.
- 25 29. The process of claim 28 wherein the reactor has two or more stages.
30. The process of claim 28 wherein the reactor has 3-30 stages.
31. The process of claim 28 wherein the reactor has 4-20 stages.
32. The process of claim 28 wherein the reactor has 8-15 stages.
- 30 33. The process of claim 30 wherein the 1,3-propanediol reactant is fed at multiple locations to the reactor.
34. The process of 30 wherein an inert gas is added to the reactor at one or more stages.
- 35 35. The process of claim 30 wherein at least some amount of steam (water vapor) that is generated as a by-product of the reaction is removed from the reactor at least one intermediate stage.

36. The process of claim 1 wherein the polycondensation is carried out in a counter current vertical reactor wherein and the 1,3-propanediol reactant and polytrimethylene ether glycol flow in a manner counter-current to the flow of gases and vapors.
- 5 37. The process of claim 36 wherein the reactor has two or more stages.
38. The process of claim 37 wherein the 1,3-propanediol reactant is fed at the top of the reactor.
39. The process of claim 33 wherein the 1,3-propanediol reactant is fed at multiple locations to the reactor.
- 10 40. The process of claim 1 wherein the polycondensation is first carried out in at least one prepolymerizer reactor and then continued in a column reactor, the 1,3-propanediol reactant comprises 90 weight % or more 1,3-propanediol, and in the prepolymerizer reactor the 1,3-propanediol is polymerized with the catalyst to a degree of polymerization of at least 5.
- 15 41. The process of claim 40 wherein in the at least one prepolymerizer reactor the 1,3-propanediol is polymerized with the catalyst to a degree of polymerization of at least 10 and the column reactor comprises 3-30 stages.
42. The process of claim 40 wherein in the at least one prepolymerizer reactor the 1,3-propanediol is polymerized with the catalyst to a degree of polymerization of at least 20.
- 20 43. The process of claim 41 wherein the at least one prepolymerizer reactor is a well-mixed tank reactor.
44. The process of claim 41 wherein steam generated in the at least one prepolymerizer reactor is removed and the product of the at least one prepolymerizer is fed to the column reactor.
- 25 45. The process of claim 44 wherein an inert gas is fed to the column reactor.
46. A continuous multi-stage process comprising reacting at least one reactant in a liquid phase in an up-flow column reactor, and forming a gas or vapor phase by-product wherein the gas or vapor phase by-product is continuously removed at the top and at least one intermediate stage.
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